California Environmental Protection Agency

Air Resources Board

PROCEDURE FOR DETERMINATION OF NITROUS OXIDE IN AUTOMOTIVE EXHAUST BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

Standard Operating Procedure No. MLD 136
Revision 2.0

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SOP No. MLD 136 – Procedure for the Determination of Nitrous Oxide in Automotive Exhaust by Fourier Transform Infrared Spectroscopy

1   Introduction

1.1   This document describes the measurement of nitrous oxide (N_2O) in vehicle exhaust using Fourier transform infrared (FTIR) spectroscopy. Although FTIR spectroscopy has been used to monitor ambient nitrous oxide concentration in peer reviewed studies (Galle et al., 1994; Griffith and Galle, 2000) and in an US Environmental Protection Agency (EPA) sponsored study (Eklund and LaCosses, 1998), no other standard operating procedure has been written (by either the US EPA or CalEPA) for the determination of nitrous oxide using FTIR.

1.2   For routine motor vehicle testing, the vehicle is tested according to the Federal Test Procedure (FTP, see CFR title 40), using a dynamometer (dyno) and a constant volume sampler (CVS) to dilute the exhaust for sampling.

1.3   Samples are also received from CVS testing using non-FTP driving cycles, Sealed Housing Evaporative Determinations (SHEDs), gas cylinders, and miscellaneous sources supplied in Tedlar bags or canisters.

1.4   In addition to nitrous oxide, the FTIR is also calibrated for other exhaust components (see step 9.2 in the calibration section). These additional calibrations allow routine comparisons between values obtained by the FTIR versus those reported by standard dynamometer instruments for the purpose of quality control.

1.5   This method is applicable for nitrous oxide determination in the range of 0.1 to 10 ppm v/v.

2   Method Summary

2.1   Routine motor vehicle testing is performed on a dynamometer according to a standard test cycle, and the exhaust is diluted with a CVS.

2.2   Diluted exhaust is collected in Tedlar bags and analyzed by FTIR after the vehicle test.

2.3   Infrared (IR) spectra are obtained by splitting an infrared beam with a potassium bromide (KBr) beamsplitter, reflecting one beam at a fixed mirror and the second beam at a moving mirror. When recombined, interferences between the two beams are recorded as an intensity versus mirror distance plot (interferogram). This interferogram is converted mathematically (Fourier transform) into an intensity versus wave number plot known as a single-beam spectrum. A single-beam spectrum of the gas exhaust sample is ratioed against a single-beam background spectrum (a scan of the evacuated gas cell) to produce an absorbance spectrum.

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2.4   Spectral absorbances at characteristic wave numbers in the 2187.6 cm^{-1} to 2205.2 cm^{-1} region are linearly proportional to the concentration of nitrous oxide (Beer's Law).

2.5   The absorbance spectrum of exhaust is a composite of the absorbances of all components, especially carbon dioxide and water which are present at percent (~10,000 ppm) levels. For each species of interest, absorption at characteristic wave numbers is compared with stored spectra measured at known concentrations (reference spectra), and the concentration of the analyte (in ppm) is calculated using Beer's Law in conjunction with a classical least squares (CLS) algorithm.

2.6   Samples are measured by evacuating the FTIR's gas cell, refilling with the content of Tedlar bags, and measuring infrared absorbance after flushing. Because each absorbance measurement (a scan) takes only a second, it is standard practice to scan repeatedly and average the results (co-add) to minimize the signal-to-noise ratio.

3   Interferences and Limitations

3.1   Quantitation of gaseous pollutants involves spectral analysis within a region of the IR spectrum characteristic of each pollutant. Any species of interest is susceptible to interference from other species that have absorption peaks within its quantitation region. Of general concern are water and carbon dioxide, which are the principal combustion products and have absorption bands throughout the IR spectrum.

3.2   Within the spectral window utilized for nitrous oxide quantitation, carbon monoxide (CO) is the exhaust component with the most prominent absorbance bands (see Figure 1).

3.3   Potential interference from carbon monoxide is minimized with the following approaches:

3.3.1   Instead of using the total absorbance from the 2187.6 cm^{-1} to 2205.2 cm^{-1} spectral region for nitrous oxide quantitation, six windows within this region (gray areas in Figure 1) are utilized. Therefore, the segments where carbon monoxide absorbance is strongest are avoided.

3.3.2   Carbon monoxide is marked as an interfering component of the 2187.6 cm^{-1} to 2205.2 cm^{-1} quantitation region in the CLS algorithm (see step 7.1).

3.3.3   The effectiveness of measures 3.3.1 and 3.3.2 was verified experimentally at ARB (see Table 1 in the Appendix).
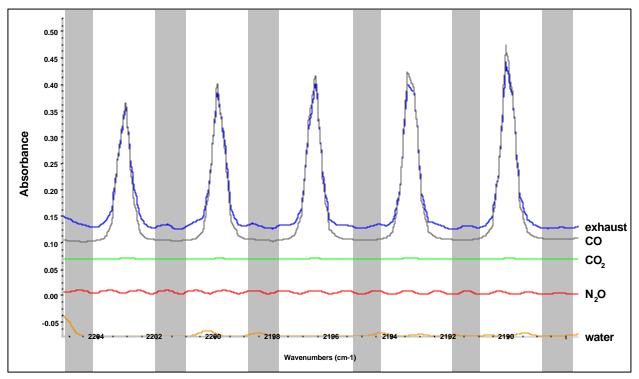
Figure 1: Spectral region used to calculate nitrous oxide concentration. An absorbance spectrum from the cold-start phase of an FTP test is shown in blue. This sample contains 1.41 ppm N_2O, 10450 ppm CO_2, 222 ppm CO, and 13510 ppm water. Four reference spectra are shown: these include 295 ppm CO (gray), 10400 ppm CO_2 (green), 1.2 ppm N_2O (red), and 27000 ppm water (brown), all in a balance of nitrogen gas. Carbon monoxide peaks clearly dominate this spectral region. The five spectra have been offset along the y-axis for visual clarity, and the six IR windows used for nitrous oxide quantitation are shaded in gray.

3.4   Carbon dioxide (green trace in Figure 1) and water (brown trace in Figure 1), are also marked as interfering components (2187.6 cm^{-1} to 2205.2 cm^{-1} spectral region) in the CLS algorithm. The following considerations also reduce the potency of these components as interferences in the quantitation of nitrous oxide by FTIR:

3.4.1   Segmentation of this spectral region into the six windows indicated in step 3.3.1 also minimizes the impact of carbon dioxide absorption peaks.

3.4.2   Synthetic mixtures of carbon dioxide and nitrous oxide, in a nitrogen background, have been analyzed at ARB (Table 2 in the appendix), and carbon dioxide's impact on nitrous oxide quantitation at representative concentrations is not significant.

3.4.3   Water vapor permeates through Tedlar bags. Diluted exhaust from an FTP vehicle test loses water steadily from time zero (in the 20,000 ppm to 30,000 ppm region) down to ambient levels (10,000 ppm or less) in about 2 hours. Nitrous oxide measurements conducted before and after water vapor

equilibration yielded the same numbers, suggesting that a two-fold change in water concentrations have little effect on measured nitrous oxide concentration.

3.5   Limitations of the CLS algorithm include the inability to compensate for absorption bands of unanticipated exhaust components, and an increase in uncertainty when several potential interferences exist within the spectral region of interest.

3.6   Unlike other oxides of nitrogen, nitrous oxide is stable in gasoline exhaust (see Figure 12 in the appendix) for at least 4 days. A sample holding time of less than 96 hours is recommended.

4   Instrumentation and Apparatus

4.1   An Nicolet Magna 560 optical bench, equipped with a Michelson interferometer, a potassium bromide (KBr) beamsplitter, and a mercury cadmium telluride (MCT) detector, is used for the analysis. Alternative FTIR instruments of similar capabilities are acceptable.

4.2   An Nicolet 10-meter multi-pass gas cell, equipped with gold-coated mirrors and a nickel-coated aluminum body, is used as the sample chamber. The IR transparent windows are made of KBr.

4.3   Measurements are made at 0.5 cm^{-1} resolution, with the gas cell at 100°C and 650 torr.

4.4   Instrument control and spectral analysis are performed with Nicolet's Omnic software or equivalent. The results are exported to other software for further processing.

5   Reagents and Materials

5.1   NIST-traceable calibration gases are used whenever possible. NIST commenced certification of gas phase nitrous oxide primary standards in 2004.

5.2   Calibration gas standards should contain no more than 1 ppm CO_2 and 3 ppm water vapor.

5.3   A purge gas is used to keep the internal optics of the FTIR free of IR absorbing species. An acceptable purge gas should be free of IR absorbing species, and contain no more than 10 ppm of CO_2 and 10 ppm of water vapor. Nitrogen gas is used at ARB.

5.4   An IR transparent gas is used as blank. Liquid nitrogen boil off or zero grade nitrogen gas is used at ARB. This blank should contain no more than 5 ppm CO_2 and 10 ppm water vapor.

5.5   A reference cylinder of nitrous oxide in nitrogen is maintained as a daily quality control standard. This cylinder must be vendor certified, with uncertainty of less than 2%, and should contain no more than 5 ppm CO_2 and 10 ppm water vapor.

5.6   A reference mixture of 100 ppm methane, 100 ppm nitric oxide, and 100 ppm carbon monoxide with nitrogen balance is used to verify proper instrument performance. This cylinder must be vendor certified, with uncertainty of less than 2%, and should contain no more than 5 ppm CO_2 and 10 ppm water vapor.

5.7   Liquid nitrogen is used to cool the MCT detector.

6   Procedure

6.1   In accordance with the manufacturer's recommendation, the FTIR is left on at all times. If instrument power down is unavoidable (i.e., power outage, relocation, or maintenance), it should be turned on at least an hour before analysis.

6.2   A steady stream of purge gas (see step 5.3 for specification) is provided whether or not the instrument is turned on. For the Nicolet Magna 560, the flow rate must be at least 10 cubic feet per hour (CFH). Other instruments may have different flow requirements.

6.3   The MCT detector is kept cool with liquid nitrogen, which is stored in a small Dewar inside the FTIR. This small Dewar is refilled at the beginning of each workday at least 30 minutes before the start of measurements.

6.4   The interior temperature of the gas cell is maintained at 100°C at all times. In case of power failure, the gas cell must be reheated to 100°C before analysis can continue.

6.5   The vacuum pump is turned on before analysis.

6.6   Start Nicolet's Omnic software. From the startup screen (Figure 2), go to the "Collect" dropdown menu and select "Experiment Setup."
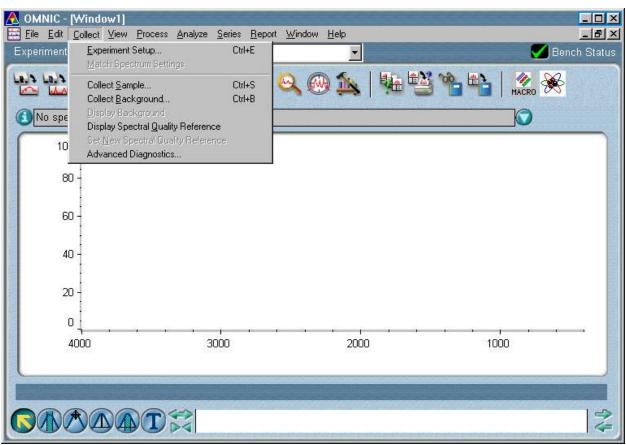
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Figure 2: The main window of Nicolet's Omnic 6.0 software. Options under the "Collect" dropdown menu are shown.

6.7   Evacuate the FTIR's gas cell and flush (fill to about 650 torr, then evacuate) twice with blank nitrogen. Within the "Experiment Setup" window, go to the "bench" folder tab (Figure 3). With a vacuum inside the gas cell, the interferogram should have a peak-to-peak height of 10-19 units. The units are meaningless save the fact that full scale is from +10 to –10, with a peak to peak height of 20. Whereas too strong of an interferogram brings risk of saturating the FTIR's analog-to-digital converter, too weak of an interferogram leads to a low signal-to-noise ratio.

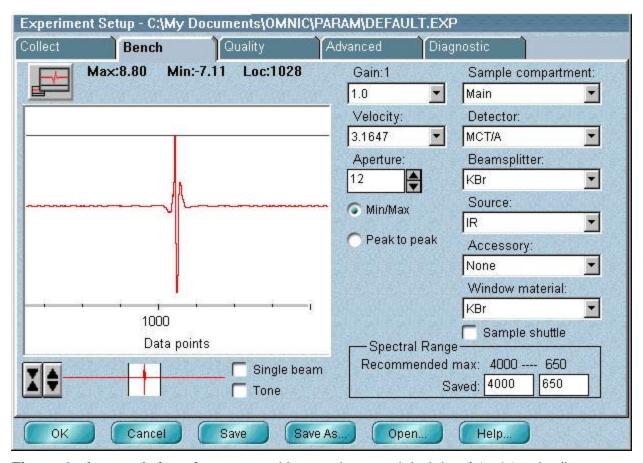**Figure 3: A sample interferogram** with a peak-to-peak height of 15.91 units (here peak height is 8.80 plus 7.11). Typical operational parameters such as detector gain, mirror velocity, aperture size, and spectral range are also shown.

6.8   Switch to the "Collect" folder by clicking on the "Collect" folder tap (Figure 4). Verify that resolution is 0.5 cm^{-1} and that the number of scans per data collection is at least 30.
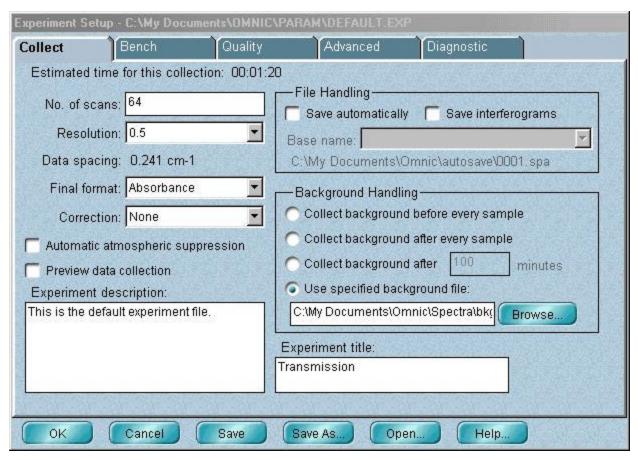
Figure 4: A sample "Collect" folder within the "Experiment Setup" screen in which 64 scans of 0.5 cm^{-1} resolution are preset for each measurement.

6.9   Exit the "Collect\Experiment Setup" screen by clicking the "OK" button.

6.10   Collect a single-beam background by selecting "Collect Background" in the "Collect" dropdown menu (see Figure 2). This single beam spectrum (Figure 5) is ratioed from all subsequent measurements before any data is stored. In the Omnic software, a single-beam background spectrum is displayed in the "% transmittance" mode.
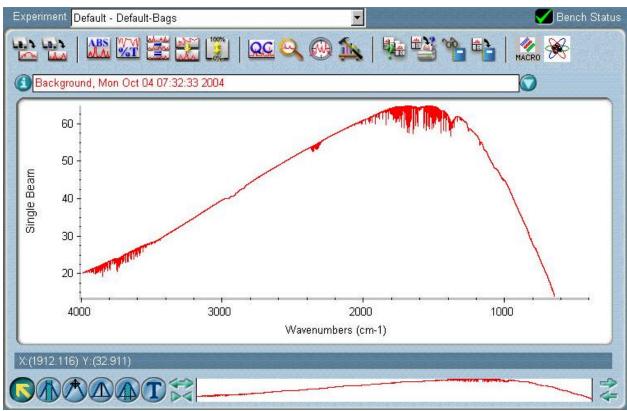
Figure 5: A typical single-beam background spectrum. Note trace amount of water (4000 to 3500 cm^{-1} and 2000 to 1400 cm^{-1}) and carbon dioxide (2400 to 2300 cm^{-1}) is still detectable. This is normal, and the background will be ratioed from all subsequent measurements before any data is stored.

6.11 Fill the gas cell with nitrogen to 650 torr and collect IR spectrum by selecting "Collect Sample" from the "Collect" dropdown menu (see Figure 2). Here the Magna 560 FTIR performs the specified number of scans (Figure 4), co-adds the results into an intermediate single beam spectrum, and ratios this spectrum against the single beam background (Figure 5). An absorbance spectrum of the nitrogen gas inside the sample chamber (Figure 6, top panel) results.
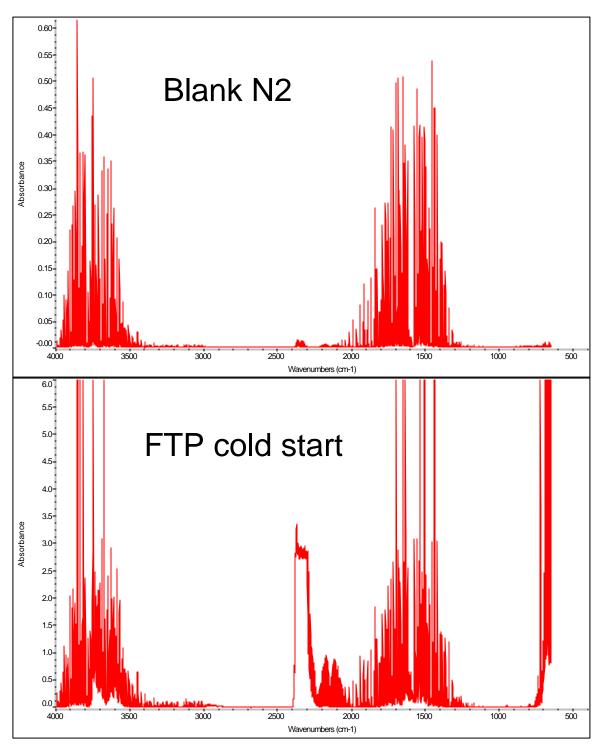
Figure 6: Typical spectra collected after selecting "Collect Sample" under the "Collect" dropdown menu. Nicolet's Omnic software displays ratioed spectra in the "absorbance" mode by default. Spectra of the Blank N2 and FTP cold start phase are collected on same analysis day. Note the ten-fold change in the y-axis and in the substantially stronger water, carbon dioxide (2400 to 2250 cm^{-1}), and carbon monoxide (2250 to 2000 cm^{-1}) signals in the "cold start" sample.

6.12   All measurements, including the single-beam background, the blank, the control standard, and the bag samples, are carried out after flushing the gas cell at least once and are co-added from at least 30 consecutive scans.

6.13   Measure the nitrous oxide concentration of the daily quality control standard.

6.14   Flush the FTIR's gas cell once with the content of a sample bag, then refill to 650 torr and measure (see Figure 6 bottom panel).

6.15   Repeat until all bags of the test cycle are measured.

6.16   Repeat until all vehicle tests of the analysis day are measured

6.17   Flush the FTIR gas cell once with blank nitrogen, than seal the chamber with nitrogen gas inside.

6.18   Turn off the vacuum pump.

7   Calculations

7.1   The classical least squared fit algorithm of Nicolet's Omnic software approximates the observed infrared spectrum with a matrix of reference spectra of both sample analytes and known interfering compounds. For each IR region of interest, this process may be expressed by the equation:

$$O = \sum_{a=1}^{m} c_a S_a + \sum_{b=1}^{n} c_b I_b + R$$

Where O, S, I, and R are vector functions representing the observed IR spectrum, the reference spectrum for the sample analyte of interest, the reference spectrum for the interfering compound, and the residual, respectively. The scalar coeffients c_a and c_b represent the concentrations of the sample analyte and of the interfering compound, respectively.

7.2   Using a c_b derived from quantitation of the interfering compound in a different IR region, the Omnic software calculates the c_a for the best fit. This concentration is then reported as ppm v/v.

7.3   A more detailed mathematical treatment is found in the "Quant setup algorithms" chapter of Nicolet's Omnic software manual.

7.4　For the quantitation of nitrous oxide, six windows with the IR region spanning the 2187.6 cm^{-1} to 2205.2 cm^{-1} are utilized, and the interfering compounds are carbon monoxide, carbon dioxide, and water (see Figure 7).
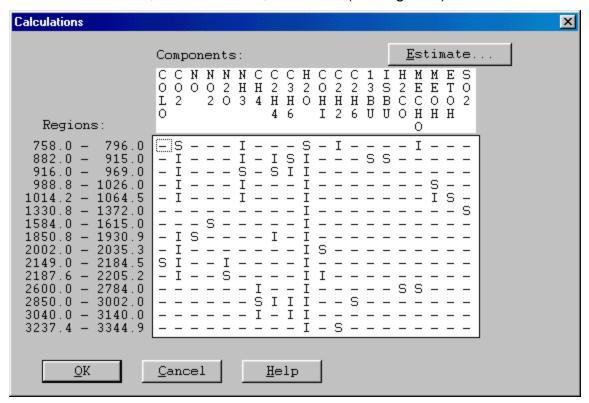
Figure 7: A sample quantitation algorithm using a matrix of 20 compounds. For each IR region indicated, the compound analyzed is mark with "S", and the interfering compound is marked with "I". Compounds that have no significant IR absorption in the region of interest are marked with "-".

8.　Data Management

8.1　The bag samples received from dynamometer tests typically include one sample for each phase of the driving cycle and one composite background. A chain-of-custody form signed and dated by a staff member of the client division must accompany each bag.

8.2　The FTIR operator signs and dates each sample bag as it is scanned.

8.2　Absorbance spectra of each sample bag are stored by Nicolet's Omnic software as a "*.spa" file. Absorbance spectra are currently named according to the following format:

　　"project number, test ID, bag ID (sequence #), date.spa"
　　　　　E.g.　2R0401, 1-EC-1, Bag1 (#1), 02-19-2004.spa
　　　　　E.g.　2R0401, 1-EC-1, Bckg (#1), 02-19-2004.spa

In the future this nomenclature may evolve in accordance with client needs.

8.3   Concentration of exhaust components (in ppm v/v) are extracted from the absorbance spectra using an appropriate CLS algorithm and pasted into a spreadsheet.

8.4   For each dynamometer test, data from the sample bags are merged into the same spreadsheet (Figure 8).

Project 2S03C1, Vehicle Test 82-EC-1, Samples, 2-04-04

TEST ID:	1010955	82-EC-1
Date	2/4/2004	

FTIR TIME	16:45		16:50		16:55	
DYNO TIME			9:11		9:26	
CO2 (Backg) - Dyno			0.046		0.045	
CO2 (Sample) - Dyno			0.464		0.286	
Blank N2	0.0253	**Blank N2**	0.0253	**Comments:**		
QC Check (6ppm)	6.0698	**QC Check (5ppm)**				

		Background		Background replicate		Phase 1		Phase 1 replicate		Phase 2	
Index	Component	Concentration	Std. error	Concentration	Std. error	Concentration	Std. error	Concentration	Std. error	Concentration	Std. error
1	Carbon monoxide low	1.6776	0.0421	1.6972	0.04015	123.641	1.32844	123.369	1.29821	18.6154	0.3501
2	Carbon dioxide	476.548	51.5149	489.899	48.722	4875.16	192.17	4885.85	195.616	3057.95	124.881
3	Nitric oxide	-0.4868	0.66457	-0.4765	0.6646	1.2933	0.64469	1.2894	0.63241	0.0638	0.66915
4	Nitrogen dioxide	3.3009	8.26821	3.2595	8.26015	3.8035	8.2339	3.8231	8.2249	3.3302	8.33272
5	**Nitrous oxide**	**0.3418**	**0.0286**	**0.3281**	**0.03561**	**0.4428**	**0.12141**	**0.47**	**0.11514**	**0.3572**	**0.05557**
6	Ammonia	0.3971	0.01765	0.3247	0.01821	0.798	0.08307	0.8531	0.08044	0.8456	0.05158
7	Methane	2.3565	0.16275	2.3206	0.1651	3.499	0.2397	3.4693	0.24267	2.4905	0.16665
8	Ethane	0.0397	0.03138	0.0124	0.03238	0.813	0.14767	0.8122	0.14301	0.1588	0.0917
9	Propane	0.0059	0.08386	-0.0344	0.08408	0.3001	0.09714	0.1491	0.10833	0.0817	0.08843
10	Water	8497.35	128.16275	8494.13	121.202	8112.71	463.303	8098.48	471.544	8421.31	305.241
11	Carbon monoxide high	1.7351	5.41549	1.1855	5.80757	122.733	7.79556	123.772	7.97953	19.5901	6.591
12	Ethane	-0.0171	0.36731	-0.1021	0.38831	0.0128	0.35777	0.2208	0.37432	-0.0019	0.35466
13	Ethane	-0.1284	0.18089	-0.1544	0.18353	0.5515	0.26489	0.5424	0.26822	-0.1676	0.18509
14	1,3-Butadiene	-0.0152	0.05662	-0.0388	0.05677	0.0166	0.06559	0.0232	0.07315	0.0088	0.05971
15	iso-Butylene	-0.0252	0.03818	0.0058	0.03828	0.0265	0.04422	0.0639	0.04932	0.024	0.04026
16	Formaldehyde	0.0857	0.07146	0.0716	0.07347	0.0045	0.06937	0.0353	0.07243	-0.0027	0.06867
17	Acetaldehyde	-0.2781	0.17285	-0.2926	0.17771	-0.0756	0.1678	-0.0526	0.17519	-0.0973	0.16611
18	Methanol	0.2153	0.91669	-0.7169	0.78936	-2.7379	1.64472	-2.1453	1.83737	-1.9824	1.35395
19	Ethanol	0.0476	0.28821	0.3249	0.2936	2.4948	1.49875	2.5747	1.46297	1.5738	0.9656
20	Sulfur dioxide	0.881	1.94716	0.9386	1.95185	1.1341	1.95267	1.1385	1.95414	0.96	1.96074

Figure 8: A sample merged raw-data spreadsheet generated with the CLS algorithm shown in Figure 7.

8.5   This spreadsheet is saved and printed, and the hardcopy is filed by date in the laboratory.

8.6   From the spreadsheet created according to 8.4, the analyst extracts concentrations of interest and applies the QC tests (see QC section below).

8.7   QC charts, QC tables, and nitrous oxide data for the entire quarter are tabulated for the quarterly QC report. This report includes verification of residual, replicate

and holding time criteria as well as crosschecks with dynamometer instrumentation (see Figure 9).

Date	Vehicle Test	Phase/Bag	MSOD Test ID	FTIR N_2O ppm	Residual ppm	relative	Replicate ppm	RPD	Replicate passing?	Residual Passing?	Proposed status	Comments
4/3/2002	2R9802, 27-EC-5	Bkgd 1	1006018	0.352	0.050	14%				Pass	DFR	
		Bkgd 2		0.346	0.050	14%				Pass		
		Bkgd 3		0.342	0.049	14%				Pass		
		Bag 1		0.551	0.170	31%				Pass		
		Bag 2		0.475	0.103	22%				Pass		
		Bag 3		0.686	0.129	19%	0.684	-0.4	Pass	Pass		
4/3/2002	2S00C1, 165-EC-1	Bkgd	1006013	0.338	0.045	13%				Pass	DFR	
		Bag 1		1.001	0.190	19%	1.004	0.3	Pass	Pass		
		Bag 2		0.973	0.136	14%				Pass		
		Bag 3		1.612	0.169	11%				Pass		
4/3/2002	2S00C1, 163-EC-1	Bkgd	1006011	0.348	0.046	13%				Pass	DFR	
		Bag 1		0.705	0.171	24%	0.706	0.1	Pass	Pass		
		Bag 2		0.424	0.136	32%				Pass		
		Bag 3		1.299	0.164	13%				Pass		
4/4/2002	2R9802, 27-EC-6	Bkgd 1	1006028	0.340	0.043	13%				Pass	DFR	
		Bkgd 2		0.335	0.044	13%				Pass		
		Bkgd 3		0.327	0.039	12%				Pass		
		Bag 1		0.598	0.178	30%				Pass		
		Bag 2		0.487	0.104	21%				Pass		
		Bag 3		0.700	0.123	18%	0.693	-0.9	Pass	Pass		
4/4/2002	2S00C1, 165-UC-1	Bkgd	1006019	0.337	0.044	13%				Pass	DFR	
		Bag 1		0.737	0.350	48%	0.752	2.0	Pass	Pass		
		Bag 2		0.890	0.190	21%				Pass		
		Bag 3		1.715	0.172	10%				Pass		
4/4/2002	2S00C1, 166-EC-1	Bkgd	1006022	0.336	0.046	14%				Pass	DFR	
		Bag 1		1.613	0.127	8%	1.609	-0.2	Pass	Pass		
		Bag 2		0.948	0.122	13%				Pass		
		Bag 3		1.890	0.143	8%				Pass		

Figure 9: An excerpt from QC worksheet containing nitrous oxide data from the second quarter of 2002.

8.8 Test samples that fail the QC criteria or the evaluation criteria are excluded from the data reported to clients.

8.9 The signed chain-of-custody forms are forwarded to the Environmental Studies and Operational Support Section of the Southern Laboratory Branch (SLB), which maintains an archive of custody records.

8.10 The storage of data files is as follows:

8.10.1 Periodically all files are copied to the division's network server.

8.10.2 The files are copied into compact disk (CD) when a threshold volume is reached, or at least once a year.

8.10.3   Files may be removed from the hard disk of the FTIR's control computer (i.e., to free disk space necessary for future analyses) as long as these files have been copied to CD.

8.11   Periodically all validated data (i.e. data for record) are reported to the VTS data base according to the following procedure:

8.11.1   A summarized version of the quarterly QC report is prepared at the end of each month to determine which data are ready for release. In contrast to the report described in 8.7, this report only includes information about residuals, replicates and crosschecks (Figure 10).

Date	Vehicle Test	Phase/Bag	MSOD Test ID	FTIR N_2O ppm	Proposed status	Comments
4/3/2002	2R9802, 27-EC-5	Bkgd 1	1006018	0.352	DFR	
		Bkgd 2		0.346		
		Bkgd 3		0.342		
		Bag 1		0.551		
		Bag 2		0.475		
		Bag 3		0.686		
4/3/2002	2S00C1, 165-EC-1	Bkgd	1006013	0.338	DFR	
		Bag 1		1.001		
		Bag 2		0.973		
		Bag 3		1.612		
4/3/2002	2S00C1, 163-EC-1	Bkgd	1006011	0.348	DFR	
		Bag 1		0.705		
		Bag 2		0.424		
		Bag 3		1.299		
4/4/2002	2R9802, 27-EC-6	Bkgd 1	1006028	0.340	DFR	
		Bkgd 2		0.335		
		Bkgd 3		0.327		
		Bag 1		0.598		
		Bag 2		0.487		
		Bag 3		0.700		
4/4/2002	2S00C1, 165-UC-1	Bkgd	1006019	0.337	DFR	
		Bag 1		0.737		
		Bag 2		0.890		
		Bag 3		1.715		
4/4/2002	2S00C1, 166-EC-1	Bkgd	1006022	0.336	DFR	
		Bag 1		1.613		
		Bag 2		0.948		
		Bag 3		1.890		

Figure 10: An excerpt from a nitrous oxide analysis report sent to the client division.

8.11.1.1   The summary QC report is then reviewed by a senior staff member of the SLB who authorizes the data release to VTS.

8.11.1.2   The spreadsheet containing the validated data that have been approved for release is converted into a script file that is submitted to the Mobile Source Operations Division (MSOD). This file contains the information about N_2O concentrations for each bag of each dynamometer test.

9.   Calibrations

9.1   The FTIR is delivered from the factory with a current set of calibrations for all 20 compounds listed in Figure 7. Except for compounds of interest (i.e. nitrous oxide and interfering compounds in the 2187.6 cm^{-1} to 2205.2 cm^{-1} region), these calibrations are retained for the lifetime of the FTIR.

9.2   Upon delivery, the FTIR was recalibrated with nitrous oxide, carbon monoxide, carbon dioxide, and selected compounds of interest using primary gas standards at ARB.

9.3   A reference mixture containing 100 ppm methane, 100 ppm nitric oxide, and 100 ppm carbon monoxide is analyzed at least 10 times to verify proper instrument performance.

9.4   This reference mixture is reanalyzed each time an optical component of the FTIR is replaced, or at least once per quarter. If at least one of the three concentrations differs from the average of the original analysis by greater than 5%, the FTIR is recalibrated for all compounds of interest, and 10 more measurements of the CH_4/NO/CO_2 mixture are made to establish a new benchmark.

10   Quality Control

10.1   *Blank* – A blank (nitrogen gas is used at ARB, see step 5.4) is analyzed daily.

10.1.1   Measured concentrations of nitrous oxide within this blank must be below the reporting limit, currently chosen as 0.045 ppm, or 1.5 times the usual limit of detection (LOD). The reporting limit must not be greater than 0.15 ppm, or 1.5 times the maximum allowable limit of detection (see 10.6 below).

10.1.2   If the condition in step 10.1.1 is not met, the cause must be determined and the problem must be corrected before analysis can continue.

10.2   *Control Standard* – For each analysis day, the control standard is analyzed. Measured values are plotted against time. The measured nitrous oxide concentration of the day must be within 5% of the running average. If repeated measurements (insufficient flushing is the most common cause of aberrant results) do not yield a passing quality control check, sample analysis may not continue and potential causes for this failure are investigated.

10.2.1   At the start of each quarter, the average measured concentration of the control standard from the previous quarter is used in place of the running average. This practice continues until 20 data points have been accumulated within the quarter year of record.

10.2.2   When a new cylinder of control standard is used, the vendor's assay value is used as the reference until 20 data points have been accumulated. The measured concentration must be within 10% of the vendor's assay value.

10.3   *Duplicates* – For each vehicle test, one of the bags must be sampled and analyzed twice. The allowable relative percentage difference (RPD) between the two measurements depends on the average concentration of the duplicate runs, as shown in the following table:

Average Concentration of Duplicate Runs	Allowable RPD
1 to 10 times the limit of detection (LOD)	30%
10 to 50 times LOD	10%
Greater than 50 times LOD	5%

10.3.1   If the RPD between these two measurements is greater than the allowable RPD, the nitrous oxide measurements are invalid and must be repeated. If the repeated measurements continue to fail this replicate QC, sample analysis may not continue and potential causes for this failure are investigated.

10.3.2   If there is insufficient exhaust sample within the set of Tedlar bags for a duplicate measurement, a duplicate measurement from another vehicle test of the same day may be used as substitute.

10.4   *Residual* – Nicolet's Omnic software reports a residual factor, a reflection of the goodness of fit achieved with the CLS algorithm (see step 7.1), as ppm nitrous oxide equivalent. If this value is greater than 50% of the reported nitrous oxide concentration, the analysis is invalid.

10.5   *Holding Time* – For each vehicle test, nitrous oxide results may be released as data of record (DFR) only if all bag samples are analyzed within 96 hours of sample collection and all other QC criteria are met.

10.6   *Exhaust sample Cross-check* – Carbon dioxide concentrations measured with the FTIR are compared with those measured with the dynamometer instruments (dyno results) in order to detect sampling errors such as bag leak and bag mislabeling.

10.6.1   For a diluted exhaust sample the FTIR results must be within 15% of the dyno result. For a background sample, the FTIR results much be within 35% of the dyno result.

10.6.2   Nitrous oxide results for a vehicle test cannot be DFR if any of four bag samples fail to comply with the conditions specified in step 10.6.1.

10.7   Linearity and limit of detection (LOD) determinations are performed each time the FTIR is recalibrated (see step 8.4), or at least once per year.

10.8   *Linearity* – For a linearity determination, at least five concentrations of N_2O are prepared using a gas divider. Each concentration level is measured at least twice.

10.8.1   The averages of measurements at each concentration are plotted against the expected concentrations based on the vendor's assay value. The coefficient of correlation, R, is calculated from the resulting linear regression (Figure 9).

10.8.2   The minimum linearity requirement is an R value no less than 0.995.

10.9   *Limit of Detection* – For a more realistic simulation of exhaust sampling conditions, the LOD determination is performed with ambient air rather than with pure gas mixtures. Worldwide ambient nitrous oxide concentrations are reported to be 0.3 ppm (Dasch, 1992;Griffith and Galle, 2000).

10.9.1   Ambient air is flowed continuously into the gas cell of the FTIR, with a flow rate of 5 liters per minute and an interior chamber pressure of 650 torr.

10.9.2   At least five measurements are made; each consecutive measurement spaced no less than 1 minute apart and no more than 5 minutes apart.

10.9.3   The LOD is calculated from the standard deviation (denoted by "s") of these measurements. It is defined by the equation:

$$\boxed{LOD = t \times s}$$

where "t" is the student's *t* value at the 99% confidence level, given by the following table:

# measurements	Degrees of Freedom	t-value
5	4	3.7
6	5	3.4
7	6	3.1
8	7	3

10.10   Nitrous oxide determinations from vehicular exhaust can only be reported if they are at or above the limit of detection. The maximum allowable LOD is 0.1 ppm.
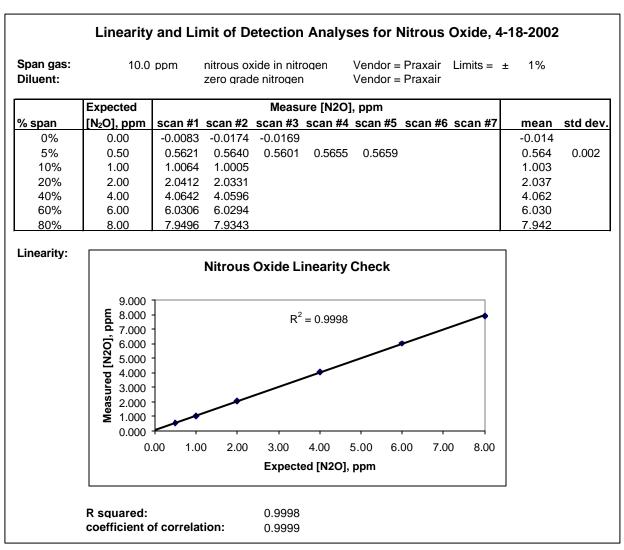
Linearity and Limit of Detection Analyses for Nitrous Oxide, 4-18-2002

Span gas: 10.0 ppm   nitrous oxide in nitrogen   Vendor = Praxair   Limits = ±   1%
Diluent: zero grade nitrogen   Vendor = Praxair

% span	Expected [N2O], ppm	scan #1	scan #2	scan #3	scan #4	scan #5	scan #6	scan #7	mean	std dev.
0%	0.00	-0.0083	-0.0174	-0.0169					-0.014	
5%	0.50	0.5621	0.5640	0.5601	0.5655	0.5659			0.564	0.002
10%	1.00	1.0064	1.0005						1.003	
20%	2.00	2.0412	2.0331						2.037	
40%	4.00	4.0642	4.0596						4.062	
60%	6.00	6.0306	6.0294						6.030	
80%	8.00	7.9496	7.9343						7.942	

The header "Measure [N2O], ppm" spans scan #1 through scan #7.

Linearity:

Nitrous Oxide Linearity Check

$R^2 = 0.9998$

R squared: 0.9998
coefficient of correlation: 0.9999

Figure 11: A sample multipoint calibration in which the coefficient of correlation is 0.9999.

11   References

11.1   California Air Resources Board, 2002. Standard Operating Procedure MLD-132 (Procedure for motor vehicle emission data management).

11.2   ***Code of Federal Regulations*** (CFR), Title 40, Part 86.

11.3   Dasch, J. M., 1992. Nitrous oxide emissions from vehicles. ***Journal of Air and Waste Management Association*** **42**, 63-67

11.4   Eklund, B., and LaCosse, J., 1998. Field measurement of greenhouse gas emission rates and development of emission factors for wastewater treatment, ***EPA Project Summary* (EPA/600/SR-97/094)**

11.5   Galle, B., Klemedtsson, L., and Griffith, D. W. T., 1994. Application of a Fourier transform IR system for measurements of N_2O fluxes using micrometeorological methods, an ultralarge chamber system, and conventional field chambers. ***Journal of Geophyical Research* 99 (D8)**, 16575-16583

11.6   Griffith, D. W. T., and Galle, B., 2000. Flux measurements of NH_3, N_2O and CO_2 using dual beam FTIR spectroscopy and the flux-gradient technique. ***Atmospheric Environment* 34**, 1087-1098

11.7   Thermo-Nicolet Corporation, 1995. Omnic software user's manual.

12   Appendix

N$_2$O ratio	Predicted [N$_2$O]	Diluent = zero N$_2$		9499 ppm CO in N$_2$		relative difference
		[CO]	[N$_2$O] observed	[CO]	[N$_2$O] observed	
5%	0.50	0	0.560	9024	0.627	11.9%
10%	1.00	0	0.968	8549	1.038	7.2%
20%	2.00	0	1.936	7599	1.988	2.7%
40%	4.00	0	3.881	5699	3.941	1.6%
60%	6.00	0	5.822	3800	5.816	-0.1%
80%	8.00	0	7.754	1900	7.696	-0.7%
N$_2$O ratio	Predicted [N$_2$O]	Diluent = zero N$_2$		2294 ppm CO in N$_2$		relative difference
		[CO]	[N$_2$O] observed	[CO]	[N$_2$O] observed	
5%	0.50	0	0.560	2179	0.520	-7.3%
10%	1.00	0	0.968	2065	0.927	-4.2%
20%	2.00	0	1.936	1835	1.891	-2.3%
40%	4.00	0	3.881	1376	3.848	-0.8%
60%	6.00	0	5.822	918	5.795	-0.5%
80%	8.00	0	7.754	459	7.738	-0.2%
N$_2$O ratio	Predicted [N$_2$O]	Diluent = zero N$_2$		497 ppm CO in N$_2$		relative difference
		[CO]	[N$_2$O] observed	[CO]	[N$_2$O] observed	
5%	0.50	0	0.560	472	0.564	0.6%
10%	1.00	0	0.968	447	0.986	1.9%
20%	2.00	0	1.936	398	1.946	0.5%
40%	4.00	0	3.881	298	3.892	0.3%
60%	6.00	0	5.822	199	5.826	0.1%
80%	8.00	0	7.754	99	7.779	0.3%

Table 1: Quantitation of nitrous oxide by FTIR is not sensitive to concentrations of carbon monoxide found in typical diluted automotive exhaust. A reference standard of 10 ppm nitrous oxide in nitrogen is diluted by either zero grade nitrogen or one of three (9499 ppm, 2294 ppm, or 497 ppm) reference standard grade carbon monoxide in nitrogen, and the resulting mixture is assayed for N$_2$O concentration using the FTIR. In typical vehicle exhaust analyses conducted at ARB, the highest observed carbon monoxide output is less than 2000 ppm.

N_2O ratio	Predicted $[N_2O]$	Diluent = zero N_2		95100 ppm CO_2 in N_2		relative difference
		$[CO_2]$	$[N_2O]$ observed	$[CO_2]$	$[N_2O]$ observed	
10%	1.00	0	0.968	85590	0.772	-20.3%
20%	2.00	0	1.936	76080	1.788	-7.7%
40%	4.00	0	3.881	57060	3.786	-2.4%
60%	6.00	0	5.822	38040	5.776	-0.8%
80%	8.00	0	7.754	19020	7.721	-0.4%
N_2O ratio	Predicted $[N_2O]$	Diluent = zero N_2		47600 ppm CO_2 in N_2		relative difference
		$[CO_2]$	$[N_2O]$ observed	$[CO_2]$	$[N_2O]$ observed	
10%	1.00	0	0.968	42840	0.870	-10.1%
20%	2.00	0	1.936	38080	1.871	-3.4%
40%	4.00	0	3.881	28560	3.834	-1.2%
60%	6.00	0	5.822	19040	5.790	-0.5%
80%	8.00	0	7.754	9520	7.719	-0.5%

Table 2: Quantitation of nitrous oxide by FTIR is not sensitive to concentrations of carbon dioxide found in typical diluted automotive exhaust. A reference standard of 10 ppm nitrous oxide in nitrogen is diluted by either zero grade nitrogen or one of two (95100 ppm or 47600 ppm) reference standard grade carbon dioxide in nitrogen, and the resulting mixture is assayed for N_2O concentration using the FTIR. In typical vehicle exhaust analyses conducted at ARB, the highest recorded CO_2 emission was below 20000 ppm.

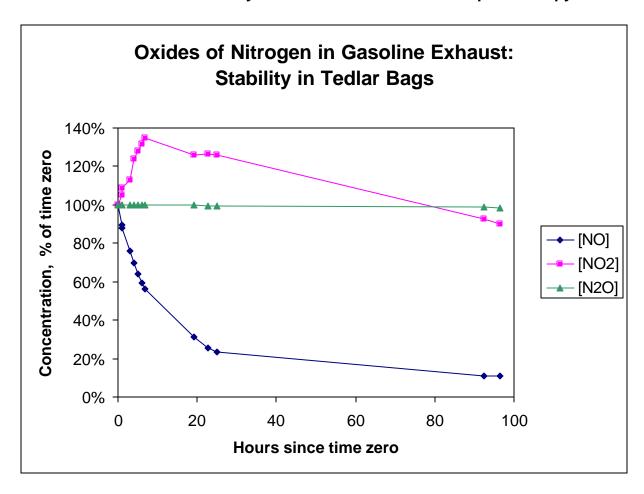## Oxides of Nitrogen in Gasoline Exhaust: Stability in Tedlar Bags

Figure 12: Stability of nitrous oxide in vehicle exhaust. CVS-diluted exhaust from a gasoline-powered vehicle was spiked with additional N_2O and monitored over time. Whereas the concentrations of both nitric oxide and nitrogen dioxide changed substantially with time, the concentration of N_2O ([N_2O]) held steady. Results from two experiments, both performed at ARB, contributed to the chart above. [N_2O] dropped by less than 0.2% after 7 hours in the first experiment, and by less than 2% after 96 hours in the second experiment.